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APPLICANTS: Kiyoshi Iseki, *et al.*

SERIAL NUMBER: 09/500,132

FILED: February 8, 2000

FOR: FUNCTIONAL ROLL FILM AND VACUUM EVAPORATION
APPARATUS CAPABLE OF PRODUCING THE FUNCTIONAL
ROLL FILM

GROUP ART UNIT: 1772

EXAMINER: Catherine A. Simone

Docket No. : 11197/1

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DECLARATION UNDER 37 C.F.R. § 1.132

Sir:

I, **Kiyoshi Iseki**, hereby declare the following:

1. I am a co-inventor of the subject matter disclosed and claimed in U.S. Patent Application Serial No. 09/500,132, filed February 8, 2000, entitled "FUNCTIONAL ROLL FILM AND VACUUM EVAPORATION APPARATUS CAPABLE OF PRODUCING THE FUNCTIONAL ROLL FILM."

2. I have read the Office Action from the United States Patent & Trademark Office (USPTO) dated February 2, 2006 and the references cited therein.

3. A method for producing a gas barrier film with a MgO-SiO₂ layer disclosed in Matsuda, JP 06-330318, published November 11, 1994, ("Matsuda") is described below.

The materials MgO and SiO₂ were vapor deposited in JP06-330318 by Matsuda, while the materials Al₂O₃ and SiO₂ used in Misano were used in the present experiment.

Al₂O₃ and SiO₂ were put into different crucibles for vapor deposition, and the materials were heated with a single electron gun in a time divided manner.

E5100, made by Toyobo Co., Ltd. (PET: 12 μm ; width of film: 1100 mm) was used as the film, and vapor deposition was carried out at a rate of 100 m/min.

4. A method for monitoring the thickness of the MgO-SiO_2 layer of the gas barrier film disclosed in Matsuda is described below.

A single fluorescent X-ray monitor was installed over the center of the film in the direction (direction in width of film TD) perpendicular to the direction in which the film runs (MD).

An area of a diameter of approximately 30 mm of an $\text{Al}_2\text{O}_3\text{-SiO}_2$ film was irradiated with X-rays for excitation generated in the X-ray generation tube in the fluorescent X-ray monitor, and the generated fluorescent X-rays were measured.

The fluorescent X-ray monitor measured $K\alpha$ of Al and $K\alpha$ of Si within the generated fluorescent X-rays, so that the resulting values could automatically be converted to the value of the film thickness using the prepared calibration curve.

5. I measured the $\text{Al}_2\text{O}_3\text{-SiO}_2$ layer thickness variations on the gas barrier film of Matsuda using the above-described system as follows.

a. I produced a film using the above method of Matsuda having a width of 1100mm and a length of 16,000 m, with an $\text{Al}_2\text{O}_3\text{-SiO}_2$ based material deposited thereon.

b. I targeted a film deposition layer thickness of 20 nm and a layer composition of 40 wt%.

c. I monitored the film deposition layer thickness in the machine direction using the above method of Matsuda.

d. I measured the film deposition layer thickness of the produced film across the width of the film, i.e., in the machine direction MD, at locations -450, -300, 0, +300, and +450 mm, where 0 mm indicates the mid-width of the film, and along the length of the film, i.e., in the transverse direction TD, at 1000 m increments from 0 to 16,000m, where 0 m indicates the start of the film.

The film was rewound in the MD and cut every 1000 m, and a square of approximately 50 mm was sampled from locations -450, -300, 0, +300 and +450 in the TD (the width of film was 1100 mm and the measured width was 900 mm in the center portion).

For every case, the sample was measured using a fluorescent X-ray spectrometer, so that the composition in the film thickness could be found for each location. The calibration curve was inputted into the spectrometer in advance.

e. Table 1 shows the distribution of the film deposition layer thickness, as measured, in the MD and the TD of the film produced according to the method of Matsuda.

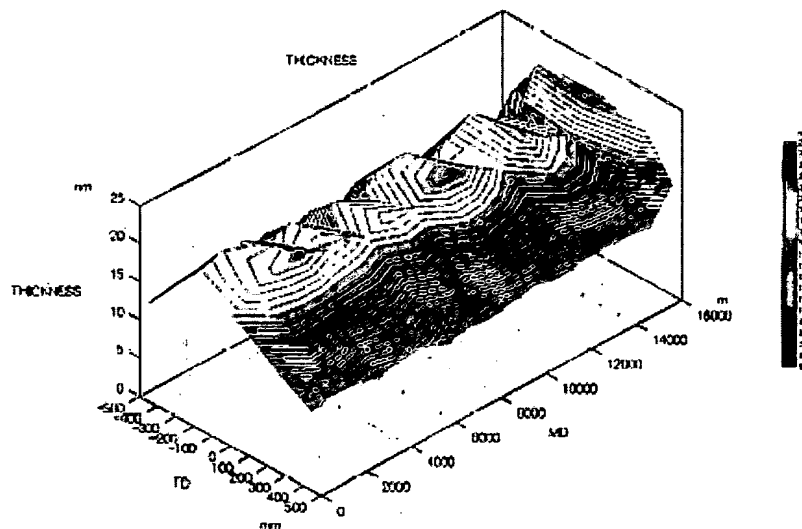
Table 1.

Machine Direction (MD),mm	Transverse Direction (TD), m																
	0	1000	2000	3000	4000	5000	6000	7000	8000	9000	10000	11000	12000	13000	14000	15000	16000
-450	13	14	14	14	13	14	12	14	12	14	15	12	13	14	12	12	15
-300	17	17	18	18	16	17	15	17	16	18	18	16	17	19	17	16	21
0	17	19	20	20	19	19	18	19	19	20	21	19	17	20	18	17	21
300	12	14	14	13	14	14	13	14	13	15	14	14	14	15	15	14	19
450	10	11	11	10	11	11	9	10	10	10	11	10	11	11	11	10	15

f. As shown in Table 1, while some sections of the film (highlighted) have thicknesses close to the target thickness of 20 nm, the majority of the sections have thicknesses that are outside the target thickness and that vary significantly from section to section. This demonstrates that a Matsuda film is unlikely to have a layer thickness ratio of 1.5 along the width and length of the film, as in the claimed film of the present invention.

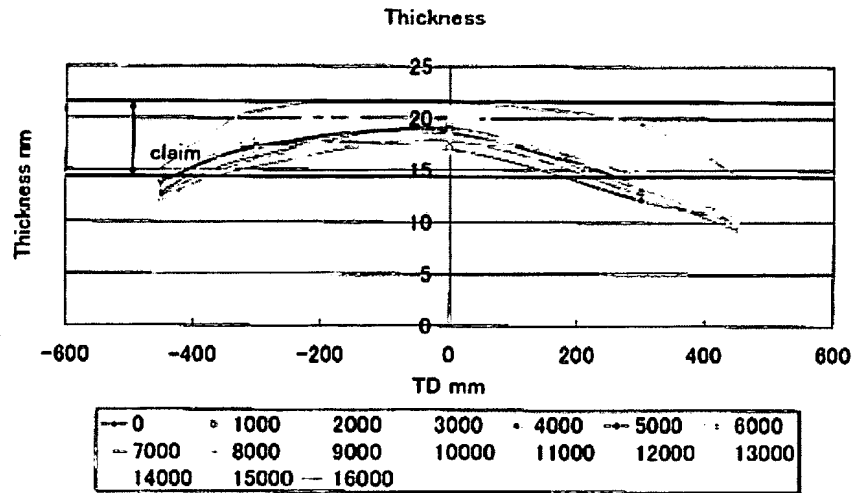
g. Figure 8 shows a three-dimensional distribution of film deposition layer thickness in the MD and TD of the film produced according to the method of Matsuda.

Figure 8.



h. Figure 9 shows the distribution of film deposition layer thickness in the TD for respective points in MD.

Figure 9.



i. As shown in Figures 8 and 9, a high level of uniformity of film layer thickness over a great width and a great length of the film can not be achieved in a film produced according to a method of Matsuda. Monitoring the film thickness in the MD alone cannot make the film layer thickness uniform because uniformity along the MD does not necessarily ensure uniformity along the TD, which is not monitored in Matsuda.

6. Based on the results shown above, using the method of Matsuda, thickness of the $\text{Al}_2\text{O}_3\text{-SiO}_2$ layer of the gas barrier film can not be kept uniform in the range as achieved by the claimed invention of this application. This non-uniformity may be at least due to the lack of thickness monitoring in the TD in Matsuda. Therefore, when Matsuda discloses a uniform layer thickness, it is not so uniform that the thickness variation ratio is 1.5 or less.

I, **Kiyoshi Iseki**, declare under penalty of perjury that the above statements are true and correct to the best of my knowledge, information, and belief. I understand that willful false statements and the like are punishable by fine or imprisonment or both (18 U.S.C. § 1001) and may jeopardize the validity of the application or any patent issuing thereon.

Declaration under 37 C.F.R. § 1.132
U.S. Application No. 09/500,132
Atty. Docket No. 11197/1

Respectfully submitted,

Date: 25/07/06

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TRANSPARENT BARRIERS FOR FOOD-PACKAGING

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ABSTRACT

Evaporated transparent silica based barriers on polymer films are providing a lot of advantages in food packaging, e.g. microwave-ability and optical transparency. Finally with intensified laws against environmental pollution by metals, the silica barrier will be the food package of the future.

Highly efficient coating of metal oxides needs a new process technique, since the physical properties like vapor pressure and evaporation - not from the liquid but from the solid state - are completely different. Additionally as SiO_2 has no barrier properties, SiO has to be reactively evaporated to get a SiO_x -($1.5 < x < 2$) coating with barrier properties. The physical properties of such transparent barriers and their production technique are discussed in this paper.

INTRODUCTION

Vacuum coating of polymer films with transparent metal oxides to improve the barrier properties for e.g. oxygen and water vapour is well known since 1964.

As the enduser-market's demands are low and a low cost production technology was not available in the past, these products were not successful on the market.

Spreading of microwave ovens in nearly all households in USA and Japan is strongly increasing the demand for a microwavable food packaging. This coated film should have the similar functional properties as Aluminium coated films concerning laminate structure and barrier properties for oxygen, water vapour and aromas.

No 1
With the development of production-save high power electron beam guns the necessary tool is available for economical coating of polymer films with transparent barriers. In this paper the properties of SiO_x -coated films and their coating technology are discussed.

PROPERTIES OF ALUMINIUM-COATINGS ON POLYMER FILMS

Before the properties of SiO_x -coatings are discussed, one should present the state of the art for Aluminium barriers for comparison.

Today Aluminium barriers are commonly produced by vacuum evaporation of Aluminium from intermetallic boats.

The coating speed is limited to app. 5 m/s, depending on the uniformity requirements. This limitation is overcome by using line-electron-beam guns as the evaporation source. Furthermore, as the electron beam is scanned on the surface of the liquid pool of Aluminium, one can improve the coating uniformity even in transverse direction to the web by using a closed loop computer control system. Web speeds of more than 10 m/s have been achieved with an uniformity better than $\pm 5\%$ for barrier coatings.

Table I: Process data and barrier properties of Aluminium barriers

	Boat ev.	EB-ev.
Substrate	PET 12 μm	PET 12 μm
Coating thickness	OD 2.9	OD 2.9
Web speed m/s	~ 5	> 10
Uniformity	± 10	$\leq \pm 5\%$
O_2 -permeation cc/m ² d bar	< 1	~ 0.5
Coating costs c/m ²	1 - 2	1 - 2

Table I represents the main results for Aluminium barriers, coated by thermal evaporation and EB-evaporation. At the same coating thickness the barrier properties of the EB-evaporated films are slightly better.

The main oxygen permeation is taking place through "pin windows", which are little uncoated surfaces on the film [2]. As the energy of EB-evaporated Aluminium vapour is higher, the structure of the layers are more dense with less pin-windows, which provides better barrier properties.

PROPERTIES OF SiO_x -COATINGS ON POLYMER FILMS

SiO_x -coatings are made by evaporation of Silicon-monoxide ($x=1$)- either by thermal or by EB-gun evaporation.

As SiO is sublimating from the solid state and not evaporating from a liquid surface, a special crucible is necessary.

For reasonable web speeds of some m/s, as it is necessary for an economical production at reasonable costs, an evaporation temperature of app. 1350°C is necessary. The vapour of SiO is oxidized in a controlled reactive atmosphere to achieve at the deposited film a degree of oxidation between $x = 1.5$ to 1.8 .

In general SiO_x -layers are relatively ductile as the coating thickness is less than 1000 \AA . As SiO_x is chemically inert, it is corrosion resistant and its properties are not negatively influenced by water during retorting [3], as it is necessary for some applications. Furthermore it is printable and not corrosion affected by the inks. [4]

Physically the deposit consists of a mixture of SiO , Si_2O_3 and SiO_2 and has therefore a slightly yellowish appearance.

In contrary to evaporated Aluminium, which has a microcrystalline structure, SiO_x is deposited as a glassy network and therefore x-ray amorphous.

The transparency and the barrier properties are mainly influenced by the coating thickness and the content of oxygen as discussed below.

The experimental work has been done on a commercial 1200 mm EB-machine with several point-sources and was confirmed on a 2000 mm line source production machine at high web speeds (4 m/s).

Additionally SiO_2 has been eb-evaporated and sputter deposited for comparison the behavior to the sub-oxides.

The general behavior of the oxygen permeation vs. coating thickness is similar to the Aluminium barriers (Fig. 1). With increasing coating thickness the oxygen permeation is decreasing drastically.

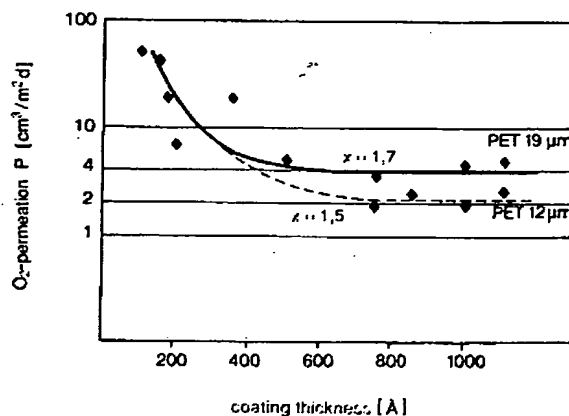


Fig. 1: Oxygen permeation vs. coating thickness for SiO_x -coated PET film

The decrease of the oxygen permeation at a thickness below 400 \AA is mainly influenced by the area which is coated with SiO_x . As the polymer film is nearly completely coated at an average thickness of app. 600 \AA , the barrier is not improved by further layers of SiO_x .

In Fig. 1 two different stoichiometric SiO_x -layers on two different PET-films are given.

Even at the tinner polyester film (12 μ), the barrier of the lower degree of oxidation is improved.

To get a clearer picture of the dependance of the barrier with changing of the content of oxygen, one set of samples has been prepared under different partial pressures of oxygen. As to be seen in Fig. 2, the permeation is drastically increasing with increasing content of oxygen.

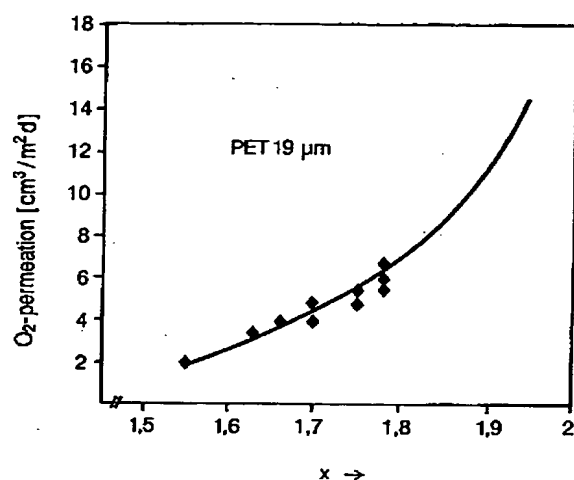


Fig. 2: Oxygen permeation of SiO_x -coated PET 19 μm vs. x

Finally silicon dioxide ($x=2$) has absolutely no barrier properties, neither made by reactive evaporation from SiO nor by evaporation from SiO_2 . Moreover sputtered SiO_2 coatings, which should have a more dense structure, are showing no barrier properties, i.e. the oxygen permeation of an uncoated film is identical to the permeation of an SiO_2 -coated film.

As SiO_2 coatings are completely penetrated by oxygen, this transport mechanism must be different from the mechanism of Aluminium-coated films.

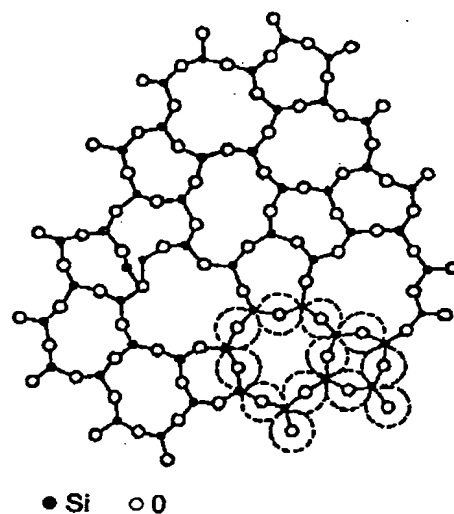
On the Aluminium-coated films most of the oxygen penetrates through the pin-windows - the uncoated point defects and through grain boundaries.

In summary about 1% of the surface is not coated and therefore the oxygen permeation is reduced to about 1%, comparing to the uncoated film.

Even if the SiO_2 -coatings are porous [5] with a lot of cracks and uncoated pin windows, one should expect some reduction of permeation by the SiO_2 -layer. But as the SiO_2 -coating has absolutely no barrier properties, the oxygen must penetrate the SiO_2 by itself. This is obvious, if one looks at the structure of SiO_2 glassy network (Fig. 3).

It consists of big hexagonal rings i.e. the layer mainly consists of micropores like switzerland cheese and it is very easy for the oxygen molecules to penetrate the SiO_2 -coatings.

Fig. 3: Glassy networks of SiO_2 -layers



From this fact it is very easy to understand the permeation behavior of the SiO_x -layers (Fig. 1), as more oxygen is removed from the glassy network and more pores are closed to a diameter, which prohibits the molecules to penetrate. Therefore the barrier is increased all the more as the content of oxygen is decreased.

On the other hand, as a result of the missing oxygen, the SiO_x -coatings are becoming yellowish. This yellowish appearance, which is originated by the absorption of UV-light at unsaturated chemical bonds ("dangling bonds") is dependant on the content of oxygen and on the coating thickness. The transparency vs. wavelength of two different samples on PET are given in Fig. 4 in comparison to the transparency of an uncoated film.

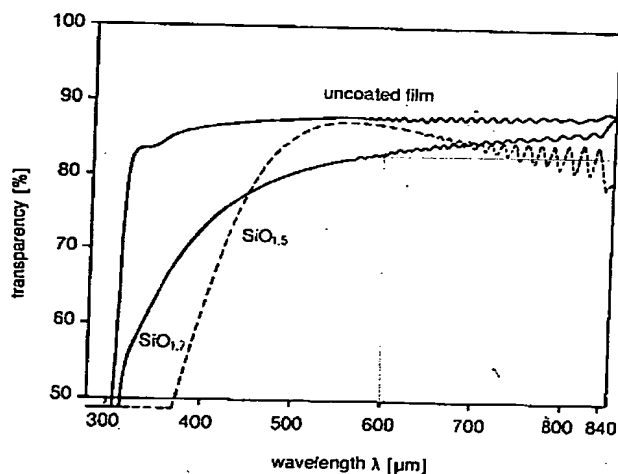


Fig. 4: Transparency vs. wavelength of two different SiO_x -samples on PET in comparison to uncoated PET.

The coating thickness of both samples is not identical, the $\text{SiO}_{1.5}$ -sample has a thickness of app. 1200 Å, the $\text{SiO}_{1.7}$ -sample only app. 800 Å. Therefore only the general behavior of the different oxygen content of the samples can be compared.

At both samples the transparency below 400 nm is strongly decreasing, which results in the yellow color of the coatings and with decreasing oxygen content the absorption below 400 nm is higher. The transparency of the $\text{Si}_{1.5}$ -coating between 450 nm and 700 nm is resulted by antireflective phenomena of the coating.

As the barrier properties and the transparency of the SiO_x -coatings are influenced by two parameters - x and coating thickness - the coating technique must be kept within a small range, even the vacuum during coating must be kept within small limits. Therefore the basic vacuum of the machine in the coating chamber has to be app. one order of magnitude better than for usual Aluminium coating and probably some reactive gas has to be added. As this technique is well experienced by reactive sputtering processes, this is no general limitation. If the vacuum level or at least the partial pressure of O_2 is controlled, the coating thickness can be controlled in-line during coating by an optical densiometer, which is working at a wavelength between 300 nm and 400 nm.

One of the main features of the SiO_x -coatings is that its barrier properties are not influenced by humidity, as given in Table II.

Table II

	O_2 -Permeation $\text{cm}^3/\text{m}^2 \text{ day atm.}$	
	0% RH	80% RH
$\text{SiO}_{1.5}$	2.8	2.8

In summary SiO_2 -coatings are providing some advantages comparing to Aluminium-barriers as they are microwavable, retortable and partially transparent. Their barrier properties are not fully satisfying and finally the coating costs are relatively high (see below).

The practical application today may be limited to some special products. Therefore the future development has

- to reduce the O_2 -permeation to a level of the Aluminium coatings
- to increase the transparency (for some applications)
- to reduce the coating costs (see below)

COATING TECHNOLOGY

The broad application of transparent barrier coatings is mainly influenced by their technical properties and their coating costs.

As the coating costs are mainly influenced by the productivity of the web coater, a process has to be chosen which allows web speeds of some m/s - comparable with the coating speeds for Aluminium coating.

To achieve coatings of app. 800 Å at high web speed, evaporation rates of 5000 - 10000 Å/s are necessary.

6

As the vapor pressure of SiO is relatively high, it can be either thermal-evaporated or electron beam-evaporated, but other metal oxides or mixtures have to be electron beam evaporated since they need temperatures of 1800° C or more to get considerably high evaporation rates.

As for SiO only temperatures of 1350° C - 1400° C are necessary to achieve web speeds of 3 - 5 m/s, a thermal evaporation technique is applicable.

In Fig. 5 a crucible for thermal evaporation of SiO is given, which has been designed as a retrofit for Aluminium web coaters.

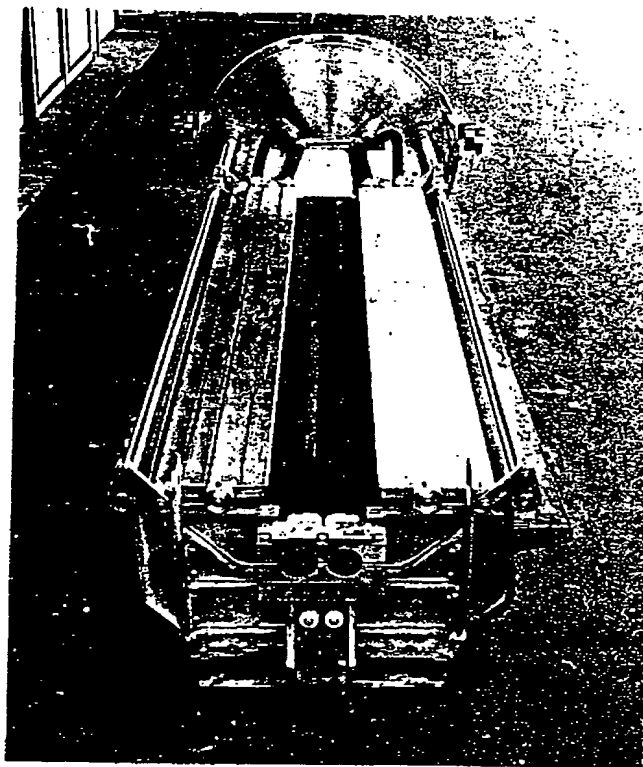


Fig. 5: Thermal evaporator for SiO

By removing the boat evaporator station for Aluminium, which is assembled as a standard at one big vacuum flange, the crucible for SiO can easily be fitted with the same vacuum flange at the same position of the Aluminium evaporator. If once modified, the exchange between both evaporators can be done in less than one day.

The evaporator mainly consists of a graphite crucible which is indirectly heated by graphite heaters. As this evaporator is a line-source, coatings of excellent uniformity are available.

This evaporator has been installed and tested with the following process parameters (Table III).

Table III: Process parameters of the SiO_x-evaporator

Substrate:	PET, 12 μ m
Coating width:	1650 mm
Evaporation temperature:	1350°-1400° C
Time for heating up:	20 min
Time for cooling down:	60-120 min
Evaporation rate:	> 100 g/min
Coating thickness:	800-1200 Å
Web speed:	100-200 m/min
Web length:	10,000-15,000 m

The main disadvantage of this evaporator is the long cooling down time. As the ingot of the crucible is limited, the web length is limited.

On the other hand this evaporator can be installed with relatively low investment costs and because of the easy exchange to the Aluminium evaporator the production of SiO_x-coated films can be adjusted to the market's demand for a pilot production.

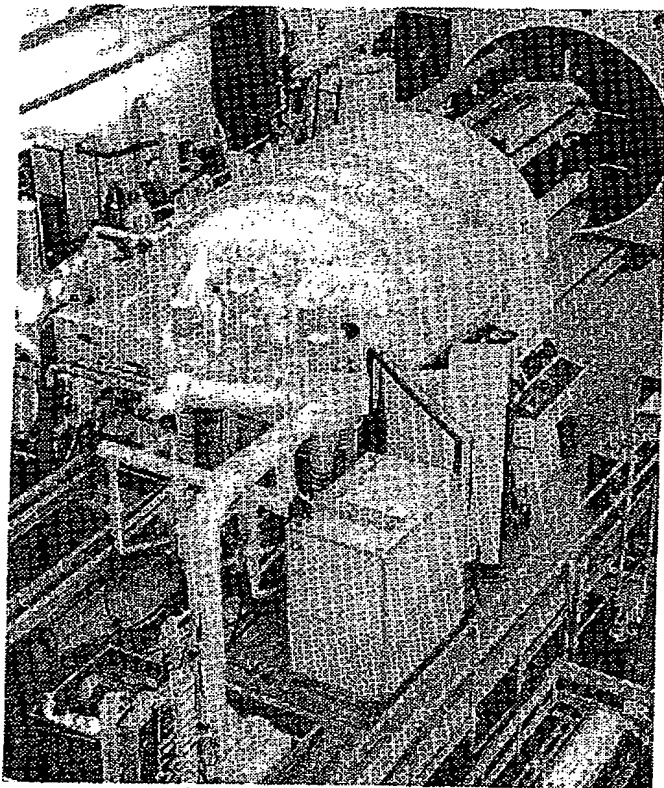


Fig. 6: General view of an universal EB-web coater with 2100 mm web width

For the highest evaporation speed of SiO and probably other ceramic materials in the future, EB-evaporation is essential. A general view on an universal EB-web coater, which is designed for evaporation of Aluminium, SiO and other materials is given in Fig. 6. With this machine the following process parameters had been achieved (Table IV).

Table IV: Process parameters of the universal EB-web coater for SiO_x-coating

Substrate:	PET, 12 μ m
Coating width:	2100 mm
Time for heating up:	20 min
Time for cooling down:	app. 5 min
Coating thickness:	800-1200 Å
Web speed:	250-360 m/min
Web length:	10,000-15,000 m

The SiO is evaporated in this machine from a watercooled crucible made of copper. As the evaporation energy is applied at the surface of the evaporant material higher web speeds are rather possible than with the thermal evaporator.

This machine is equipped with two EB-guns 200 kW, which each are micro-processor-controlled to allow a variety of scanning patterns for the different evaporation materials.

An optical thickness measurement system for Aluminium and SiO_x allows a closed loop control of the coating thickness. The total operation of the machine is computer-controlled and nearly fully-automatic. All essential process data are collected and can be printed out in roll protocol. As the crucible is mounted on a trolley a change from one evaporation material to another can be done within a few minutes. Therefore this machine is an universal flexible tool for coating of Aluminium as a basic and SiO_x-coatings as an advanced product. Even if in the future a different material as pure SiO is used for evaporation, this machine will be up-to-date.

SUMMARY

Vacuum coated transparent barriers should have a very promising future as they still have improved barriers, compared to competitive materials. The general behavior of SiO₂-based coatings is known today and a proved coating technology is available to create a market for this product. Within the next future the technical properties e.g. barrier and transparency will be improved, and a coating material will be developed to bring the coating costs in the order of magnitude of Aluminium coatings.

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A Ceramic (SiO_2 - Al_2O_3 mixture) Coated Barrier Film by Electron Beam Evaporation

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Key Words: Permeation barrier coatings
Oxides

Polymer substrates
Oxygen permeation

ABSTRACT

A ceramic (SiO_2 - Al_2O_3 mixture) coated films have low gas permeation properties. For example, typically gas barrier performances are following.

Oxygen Transmission Rate:

OTR < 1.0 (PET), 1.4 (PA) cc/m²·day·atm

Water Vapor Transmission Rate :

WVTR < 1.5g/m²·day

In addition, SiO_2 - Al_2O_3 mixture coated films have good flexibility. As a result of this property, these barrier films maintain low gas permeation after printing and lamination process.

Our developed films combine good gas barrier performances of Al_2O_3 with good flexibility of SiO_2 .

INTRODUCTION

Low gas permeation is most important property for food packaging films. This property is necessary for protecting from the oxidization or the rot of foods. It is well known that Polyvinylidene chloride (PVDC) in its various forms is the most commonly used high barrier polymer. Packaging users choose PVDC coated film for its excellent barrier property to both oxygen and moisture in the actual humidity and temperature conditions that their packages must withstand during transportation, storage, and use. However, as for PVDC, it is afraid of air pollution due to the occurrence such as dioxin in burning. Therefore recently, various ceramic-coated barrier films, e.g. SiO_x or Al_2O_3 are gaining market share in packaging. They also permit the use of metal detection systems in packaging machines. Then they have ecological advantages because of weight reduction and non-halogen.

But gas permeation must not increase after printing process, laminating process with sealant, bag making process and so on. So, it is important development target to find out new ceramic thin film, which has good flexibility.

Various ceramic-coated barrier films and its characteristics

Table I shows the various ceramic-coated barrier films and its characteristics. SiO_x -coated barrier film was almost used in early days of the development because it is comparatively easy to get barrier performance [1]. The barrier performance and the coloration are related to the value of X, and it is usually chosen as about $x=1.5$ -1.8. As for the weak point of this type, raw material costs are overly expensive and SiO_x -coated film is light yellowish, however is still main barrier material even today.

The second type is colorless transparent SiO_2 deposited by Plasma-Enhanced Chemical Vapor Deposition (PE-CVD) method. PE-CVD takes advantage of glow-discharge plasma, which decompose the raw material silane, TEOS, TMDSO and so on. In recent years, several methods of modified CVD have reported, and offer good performance) [2].

The third type is typically referred to as Al_2O_3 deposition by the reactive evaporation method. This method can achieve high deposition rates nearly equal to Al metal evaporation. One disadvantage of this material is its easy fragility in comparison with SiO_x . Recently, toughness of thin film has been reported by using plasma-enhanced evaporation [3].

The last one is the newest. In recent year several manufacturers have reported constitutions of double ceramic layer. For example [4, 5], the first layer of deposited Al_2O_3 acts to smooth the polymer surface and stimulates the growth of a second layer of SiO_2 .

We have developed a new ceramics composition and a new evaporation process using an electron beam gun to satisfy packaging film requirements. Such requirements of packaging films mean high barrier performance, good flexibility, colorless transparency and low cost. This report presents some experimental results concerning with this new transparent barrier film.

Table I. Various ceramic-coated barrier films and its characteristics.

	1	2	3	4
Material	SiO _x (x=1.5~1.8)	SiO ₂	Al ₂ O ₃	Double layer SiO ₂ /Al ₂ O ₃ SiO ₂ /SiO
Deposition Methods	Evaporation	PE-CVD	Reactive Evaporation	Evaporation
Thickness(Å)	400 ~800	150	250	500/25
OTR (cc/m ² ·day·atm)	1~2	1	2~4	2~3
Color	Yellow	Clear	Clear	Clear

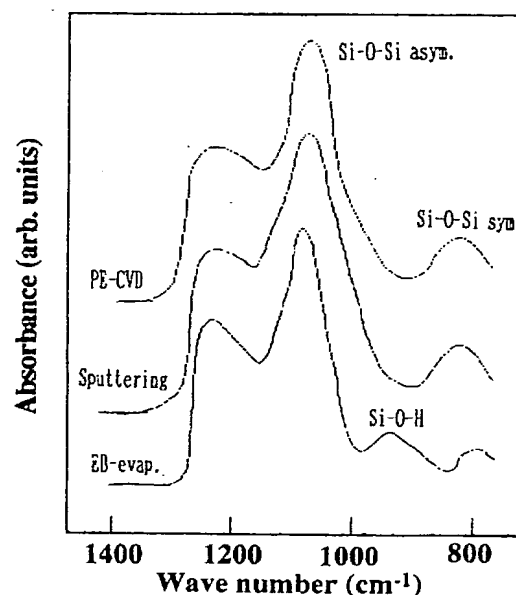
Table II. Characteristics of SiO₂ Thin Films by PE-CVD, Sputtering and EB-Evaporation

Deposition Method	PE-CVD	Sputtering	EB-Evaporation
OTR (cc/m ² ·day·atm)	4	0.5	15~70
Deposition Rate (Å/sec.)	5	1	2000
Thin Film Density (g/cc)	2.1	2.1	1.95
Si-O-H bond (930cm ⁻¹ IR absorption)	None	None	Exist

EXPERIMENTAL

In our approach, we prepared some SiO₂ layer on 12μm PET film by PE-CVD, sputtering and evaporation methods in batch-type apparatus, and analyzed them. According to Table 2, in the case of the evaporation method barrier performance was lacking, confirming this well-known fact. It must be noted that with PE-CVD and sputtering, thin film density has a high value. But the density of evaporation method is low.

In addition, Figure 1 shows infrared (IR) absorption spectrum of these SiO₂ thin films. SiO₂ thin film by evaporation has 930cm⁻¹ absorption peak. This peak doesn't exist in SiO₂ thin film by sputtering and PE-CVD. This remarkable point suggests that Si-O-H bonds exist in SiO₂ layer by evaporation. Accordingly, the thin film structure deposited by evaporation is porous. In this thin film, numerous incomplete bonds exist between Si and O atoms; thus we have to bond Si and O using other atoms or by using another deposition process. When achieved, barrier performance improved as relative material density increased and Si-O-H bonds. According to the situation described above, we tried to add various kinds of metals and metal oxides to SiO₂ to reduce the number of incomplete bonds of Si and O. Some of the various SiO₂ mixtures dissolved in boiling water and others didn't have gas barrier performance. Ultimately, combining good gas barrier performances of Al₂O₃ with good flexibility of SiO₂, we were able to develop a new colorless transparent barrier film having both high gas barrier performance and good applicability.

Figure 1. Infrared absorption spectrums of various SiO₂ thin films.

Sample making and its apparatus

Dual Element (SiO₂ and Al₂O₃) Electron-Beam Evaporation apparatus is shown in Figure 2. Al₂O₃ and SiO₂ are simultaneously vaporized by one EB-gun. Al₂O₃ and SiO₂ vapor are mixed at the gas phase in chamber, and this mixed vapor spreads to web film, and forms the barrier thin film. It is ascertained that thin film composition is homogeneous in the depth direction by Auger Electron Spectroscopy (AES: Figure 3).

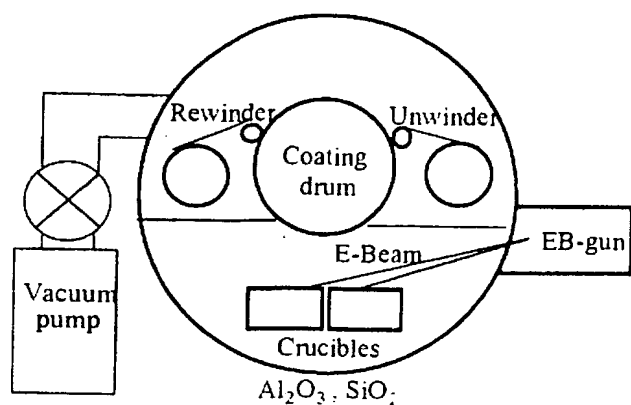


Figure 2. Schematic of Dual Element Electron-Beam Evaporation apparatus.

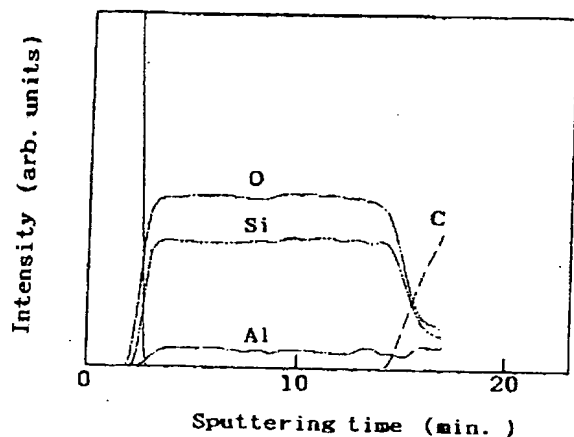


Figure 3. Depth profile of $\text{SiO}_2\text{-Al}_2\text{O}_3$ layer by AES.

EVALUATION

Relative density and IR absorption spectrum

For confirmation of deposition condition, it is very important to evaluate the dependence on relative density to Al_2O_3 content in $\text{SiO}_2\text{-Al}_2\text{O}_3$ thin film. Figure 4 shows the relation between Al_2O_3 proportion and the relative density of thin film. Relative density exceeds 95% at 30wt. % Al_2O_3 content. This relative density is equal to that of PE-CVD and sputtering. In corresponding, OTR and WVTR are improved with the proportion of Al_2O_3 content.

Figure 5 shows IR absorption spectrum of various Al_2O_3 content thin films. 930cm^{-1} peak disappear by adding Al_2O_3 to SiO_2 . 1060cm^{-1} peak which is Si-O asymmetric vibration absorption shift to low wave number. This can deduce that Si-O-Al network exists. Because Al-O bonding energy is higher than Si-O, Si-O absorption wave number in Si-O-Al network shift to low.

Relative density and IR absorption spectrum results mean that SiO_2 thin film structure become better order by Al_2O_3 addition.

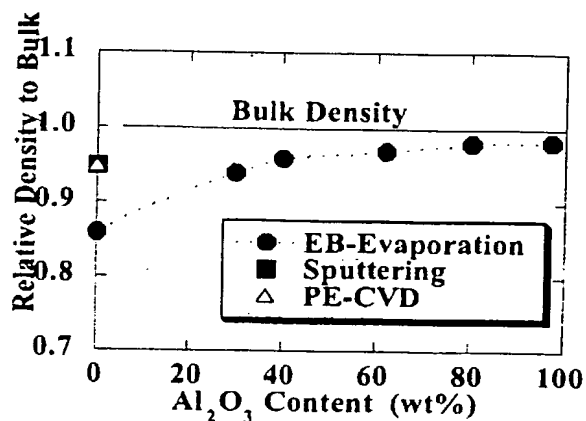


Figure 4. Thin film relative density to bulk versus Al_2O_3 contents in new ceramic layer.

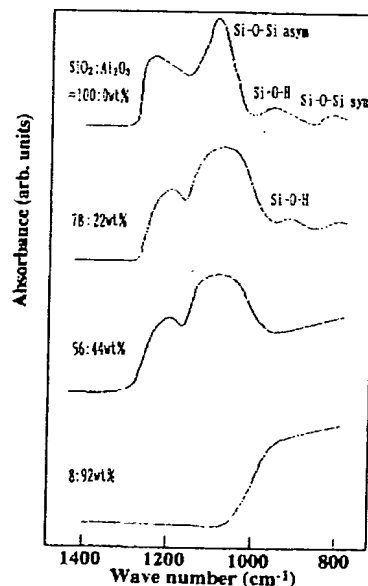


Figure 5. IR absorption spectrum of various Al_2O_3 content thin films.

Figure 6 shows Oxygen transmission rate (OTR) is less than $2\text{cc}/\text{m}^2\cdot\text{day}\cdot\text{atm}$ and water vapor transmission rate (WVTR) is less than $4\text{g}/\text{m}^2\cdot\text{day}$ above 35%. This thin film has colorless and transparency (Figure 7).

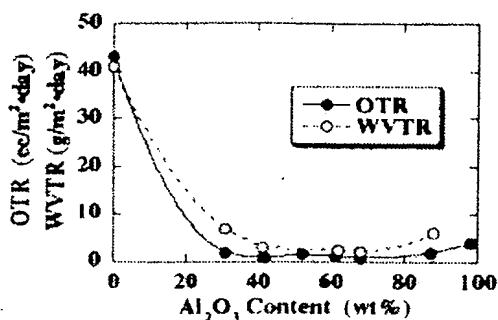


Figure 6. Oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) versus Al_2O_3 content in new ceramic layer.

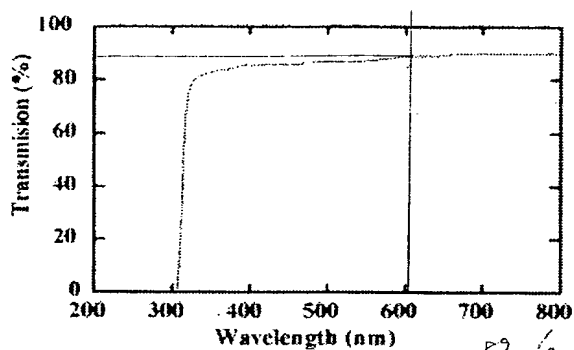


Figure 7. Transparency of new ceramic-coated 12µm PET versus light wavelength.

Flexibility

OTR dependence on stretching treatment is shown in Figure 8. The $\text{SiO}_2\text{-Al}_2\text{O}_3$ ceramic is superior to Al metal in substrate elongation. Al_2O_3 - and SiO_x -coated film is quite fragile in comparison with developed barrier film.

As these results, initial properties of $\text{SiO}_2\text{-Al}_2\text{O}_3$ coated film is suitable for packaging film. Table III collects some properties using 12µm PET film and 15µm polyamide (PA) film.

Practice property evaluation

For packaging film, gas barrier properties must keep good performance. So, we examine high humidity condition, lamination process and ink printing process.

Figure 10 shows the variations of OTR against relative humidity. The OTR of $\text{SiO}_2\text{-Al}_2\text{O}_3$ coated PET films are stable even high relative humidity region. In addition, $\text{SiO}_2\text{-Al}_2\text{O}_3$ coated PA films have same stable level to PET films in spite of PA film extend with humidity. This stability causes flexibility and elasticity of $\text{SiO}_2\text{-Al}_2\text{O}_3$ thin film.

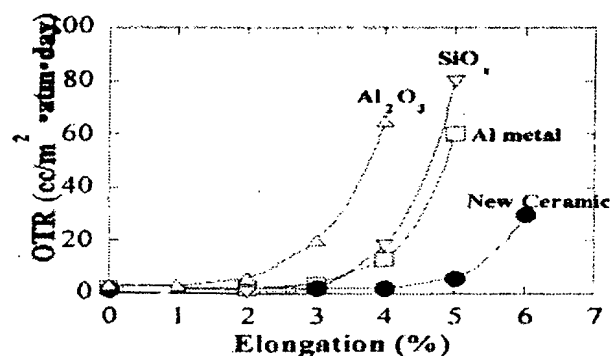


Figure 8. Oxygen transmission rate (OTR) versus elongation of $\text{SiO}_2\text{-Al}_2\text{O}_3$, SiO_x , Al_2O_3 , Al metal-coated on 12µm PET.

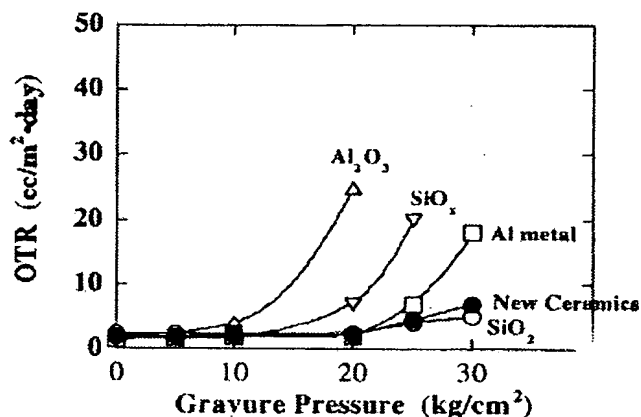


Figure 9. Gravure pressure versus OTR

Evaluation of laminated film

In an ordinary way ceramic-coated barrier films are used after lamination. To optimize laminating conditions, gravure pressure was investigated.

Figure 9 shows gravure pressure versus OTR. The properties of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ coated barrier films are sufficient achieving for practical lamination processing. As one practical test, Table III. shows the test result after lamination with PE (40µm). Lamination conditions are following:

Laminated film: PE 40µm
Adhesion: polyurethane
Film tension: 10kg/m (elongation: < 1%)
Pressure: adhesion coat 10kg/cm²:
: Lamination: 3kg/cm²

Table III. Results of $\text{SiO}_2\text{-Al}_2\text{O}_3$ Barrier Coating after Lamination with PE 40 μm .

Base film	PET	PA
Thickness	12 μm	15 μm
OTR (cc/m ² atm day)	1.0	1.4
OTR after gelbo test (cc/m ² atm day)	3.1	4.3
OTR after ink printing (cc/m ² atm day)	1.5	2.0
Color b	0.7	0.8
Adhesive - laminated strength (g/15mm)	650	580

Adhesive lamination reduces OTR by 0-200% compared with unlaminated film, and WVTR improves also. The reason for this has not yet been identified, but OTR reaches <1.0cc/m²•day and WVTR <1.5g/m²•day. In addition, the barrier performance after gelbo test is not so changed.

In addition, Table III shows gas barrier properties after ink printing process. $\text{SiO}_2\text{-Al}_2\text{O}_3$ coated films keep good barrier performance after ink printing.

From these evaluations, $\text{SiO}_2\text{-Al}_2\text{O}_3$ coated PET and PA films are suitable for packaging film.

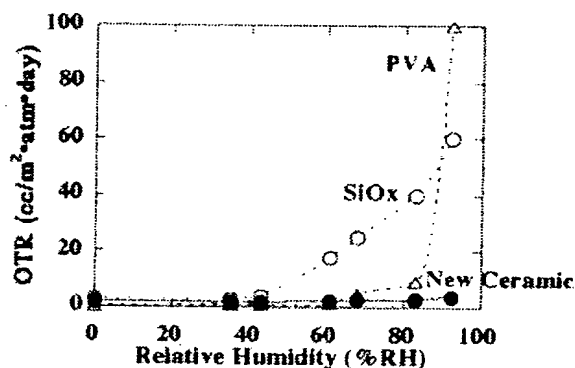


Figure 10. OTR against relative humidity of $\text{SiO}_2\text{-Al}_2\text{O}_3$ coated PA film

CONCLUSIONS

A new ceramic which is composed of SiO_2 and Al_2O_3 mixture coated on 15 μm PA and 12 μm PET film is described in this paper. The following conclusions have been reached:

1. It is possible for this new ceramic-coated 12 μm PET film to achieve OTR of less than 1.0cc/m²•day and WVTR of less than 1.5g/m²•day and also to adapt PA film.
2. The new ceramic-coated barrier film has high flexibility.
3. This barrier film offers colorless transparency.
4. This new ceramic-coated PET and PA films keep good barrier performance after high relative humidity, lamination process and ink printing process.

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